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(54) **Temperature sensitive paint composition and method of temperature determination**

(57) A paint composition including a polymeric host material and a phosphorescent material operable to phosphoresce on subjection to irradiation by laser light with the rate of decay of the intensity of the phosphorescent being a function of the temperature of the irradiated surface, is used to establish a t mperature correction factor for use of the same or a modified paint composition to improve the accuracy of measurement of pressure of oxygen over a surface which is not only pressure dependent but also temperature dependent.

The host material is preferably polyvinylidene chloride or a copolymer of vinylchloride and vinyldichloride or polyvinylalcohol, and the phosphorescent material being a porphyrin derivative or an inorganic phosphor such as yttrium oxysulphide or doped yttrium varalate.

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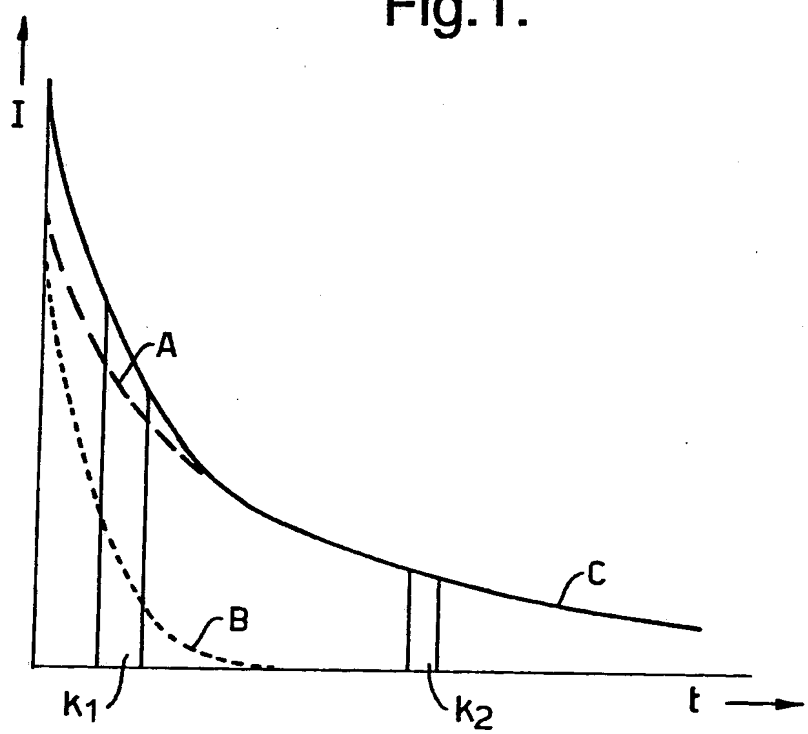
At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

Fig.1.



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TEMPERATURE SENSITIVE PAINT COMPOSITION AND METHOD OF TEMPERATURE DETERMINATION

This invention relates to a temperature sensitive paint composition and to a method of temperature determination utilising such a composition and particularly, but not exclusively, relates to such a paint composition which is either additionally pressure sensitive or which can be used in conjunction with a pressure sensitive paint to eliminate temperature errors in a pressure determination.

Paint compositions have been proposed for use to measure the partial pressure of oxygen over a surface coated with such compositions. Such proposed coatings operate such that upon irradiation with a suitable light source the coating phosphoresces. The intensity of the phosphorescence is proportional to the partial pressure of oxygen above the coating. If oxygen is present in the vicinity of the coating oxygen molecules absorb the energy of the excited phosphorescent compound in the coating and the intensity of phosphorescence is thereby reduced. Thus oxygen acts to reduce the intensity of phosphorescence and methods have been proposed for measuring the partial pressure of oxygen over the coating by measurement of the intensity of phosphorescence.

Such a proposed method and coating has been found to be unsatisfactory because the phosphorescent behaviour of the proposed coatings is also dependent upon temperature

of the surface coated. If the local temperature at the site of phosphorescence excitation is not known, as may be the case in wind tunnel experiments for which these coatings are mainly intended, then it is not possible to measure with any precision and accuracy the local pressure of oxygen over the coated surface.

There is thus a need for a temperature sensitive paint composition which can be used alone to determine temperature or which can form part of or be used in conjunction with a pressure sensitive composition to eradicate the inaccuracy producing effect of temperature on the pressure determination.

According to a first aspect of the present invention there is provided a paint composition suitable for application as a coating to a surface, which composition includes a polymeric host material and a phosphorescent material operable to phosphoresce on subjection to irradiation by laser light, with the rate of decay of the intensity of the phosphorescence being a function of the temperature of the irradiated surface.

Preferably the phosphorescent material is dissolved in the polymeric host material, which polymeric host material has a low permeability to oxygen.

Conveniently the phosphorescent material is a porphyrin derivative.

Advantageously the polymeric host material is polyvinylidene chloride, a co-polymer of vinylchloride and vinyldichloride or polyvinylalcohol.

Preferably the phosphorescent material is suspended in the polymeric host material.

Conveniently the phosphorescent material is an inorganic phosphor.

Advantageously the inorganic phosphor is yttrium oxysulphide or doped yttrium vanadate.

Preferably the polymeric host material is impregnated with phosphorescent material.

Conveniently the polymeric host material is a colloidal suspension of particles of polyvinylidene chloride or a co-polymer of polyvinylchloride and polyvinylidene chloride.

Advantageously the polymeric host material is polyvinylalcohol or hydroxy-alkylcellulose.

Preferably the paint composition includes a second phosphorescent material operable to phosphoresce on subjection to irradiation by laser light, with the rate of decay of the phosphorescence of the second phosphorescent material being a function of the pressure of oxygen over the surface.

Conveniently the polymeric host material is permeable to oxygen, the oxygen sensitive second phosphorescent host material is dissolved in the polymeric host material and

the temperature sensitive phosphorescent material is suspended in the polymeric host material.

Advantageously the polymeric host material is an oxygen permeable ethylcellulose or siloxane, the oxygen sensitive second phosphorescent material is a porphyrin dissolved in the polymeric host material, and the temperature sensitive phosphorescent material is a colloidal suspension of phosphor impregnated particles of polyvinylidene chloride or a co-polymer of polyvinylchloride and polyvinylidene chloride.

Preferably the temperature sensitive phosphorescent material is a low or non-oxygen permeable polymeric material in which is occluded a soluble phosphor, and the oxygen sensitive second phosphorescent material is an oxygen permeable polymeric material in which is occluded a material which phosphorescences on irradiation with laser light and has a decay rate which is a function of both temperature of the surface and pressure of oxygen over the surface, with the temperature sensitive phosphorescent material and oxygen sensitive phosphorescent material being a colloidal suspension in said polymeric host material.

Conveniently the soluble phosphor is a porphyrin and the oxygen permeable polymeric host material is polymethylmethacrylate.

Advantageously the paint composition is in the form of a colloidal suspension of particles having a core of

th polymeric host material which is permeable to oxygen in which is dissolved a phosphor and oxygen, which core is encapsulated in a polymeric host material substantially impermeable to oxygen.

Preferably the phosphor is a porphyrin and the substantially oxygen impermeable polymeric host material is polyvinylidene chloride.

According to a further aspect of the present invention there is provided a method of determining the temperature of a surface, including the steps of applying a coating to the surface of a paint composition as hereinbefore described, irradiating the coating with a pulse of laser light, measuring the time for decay of the intensity of the resulting phosphorescence and relating the decay time to the temperature of the surface.

According to yet another aspect of the present invention there is provided a method of determining the pressure of oxygen over a surface, including the steps of applying a coating to the surface of a paint composition as hereinbefore described, applying on top of said coating a further coating of an optically transparent paint composition which phosphoresces on irradiation with laser light and whose time for decay of the intensity of the phosphorescence is a function of both temperature of the irradiated surface and oxygen pressure over the surface, irradiating the two coatings with a pulse of laser light, measuring the time for decay of the intensity of the

resulting phosphorescence, at two parts of a plot of the intensity versus time curve, combining this information with calibration information for said two parts, and deriving therefrom the oxygen pressure and temperature at the surface.

According to yet a further aspect of the present invention there is provided a method of determining the pressure of oxygen over a surface, including the steps of applying a coating to the surface of a paint composition as hereinbefore described, irradiating the coated surface with a pulse of laser light, measuring the time for decay of the intensity of the resulting phosphorescence, at two parts of a plot of the intensity versus time curve, combining this information with calibration information for said two parts, and deriving therefrom the oxygen pressure over the surface.

For a better understanding of the present invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying single figure drawing Figure 1 which is a graphical plot of intensity of phosphorescence versus elapsed time from excitation using a paint composition according to the present invention and for use in the method of the present invention.

Paint compositions of the present invention are suitable for applications as a coating to a surface and include a polymeric host material and a phosphorescent

material operable to phosphoresce on subject to irradiation by laser light, with the rate of decay of the intensity of the phosphorescence being a function of the temperature of the irradiated surface. The paint composition can be applied to the surface in any convenient manner such as by brushing, spraying, spinning or dipping and dried in any convenient manner.

Example 1.

The composition, according to the invention, is a simple homogeneous mixture in which the phosphorescent material such as a porphyrin derivative is dissolved in the polymeric host material which has a low permeability to oxygen. Suitable low oxygen permeability polymeric host materials are polyvinylidene chloride, a co-polymer of vinyl chloride and vinyldichloride and polyvinylalcohol. The co-polymer is preferred because of its greater solubility in organic solvents and its low permeability to water vapour.

Example 2.

The paint composition according to the invention of Example 2 is a heterogeneous mixture of phosphorescent material suspended in the polymeric host material. A suitable phosphorescent material is an inorganic phosphor such as yttrium oxysulphide or doped yttrium vanadate. The phosphorescent resulting from such phosphorescent materials is relatively unaffected by oxygen and thus the

polymeric host material need not necessarily be substantially impermeable to oxygen.

Example 3.

The paint composition, according to the present invention, of this example comprises a colloidal suspension of particles of polyvinylidene chloride or polyvinylchloride-polyvinylidene chloride co-polymer which are impregnated with a phosphorescent material. The phosphorescent material which may be a porphyrin is incorporated and after stabilisation of the particles suspended in the polymeric host material. Suitable polymeric host materials, which preferable are water soluble, included polyvinylalcohol and hydroxyalkylcellulose. Again as the phosphor is occluded in the suspended particle which has a very low permeability to oxygen, the polymeric host material does not require to be of low oxygen permeability.

The compositions of Examples 1 to 3 may be made up by dissolving the polyvinylidene chloride or polyvinyl chloride co-polymer in an organic solvent such as a mixture of toluene and tetrahydrofuran, preferably a 70/30 mixture by volume, at a temperature of about 40 to 50°C. The porphyrin was added to the mixture after the polymer had dissolved, preferably at a proportion of about 1mg of porphyrin per millilitre of polymer solution. Suitable porphyrins include platinum and palladium derivatives of octaethylporphyrin and tetrakis (pentafluorophenyl)

porphyrin. The particles of polyvinylidene chloride or polyvinylchloride-polyvinylidene copolymer utilised preferably had a size within the range of from 50 nanometres (nm) to 10 micrometres (μm) and most preferably were submicron in size.

The paint compositions of Examples 1 to 3 can be adapted for use to measure both temperature and oxygen pressure. For example any one of these paint compositions based on substantially oxygen impermeable polymeric host materials could be overcoated with a paint composition that is sensitive to both temperature and pressure.

Alternatively the paint compositions of Examples 1 to 3 may be modified to produce a single paint composition which is sensitive both to temperature and to the pressure of oxygen over the surface on which they are coated. Suitable paint compositions according to the present invention are as follows:

Example 4.

This paint composition of the invention includes not only phosphorescent material sensitive to temperature only which is suspended in an oxygen permeable polymeric host material but also a second phosphorescent material operable to phosphoresce on subjection to irradiation by laser light with the decay rate of the phosphorescence of the second phosphorescent material being a function of the pressure of oxygen over the surface coated. This second

phosphorescent material is dissolved in the oxygen permeable polymeric host material.

Example 5.

This paint composition according to the present invention is a colloidal suspension of polyvinylidene chloride and phosphor in an oxygen permeable polymeric host material such as ethylcellulose polymethylmethacrylate or a siloxane, in which has been dissolved a porphyrin or other soluble phosphor.

Example 6.

This paint composition according to the present invention is a colloidal suspension of two types of particle. One type of particle is formed from a low or substantially non-oxygen permeable polymeric host material in which is occluded a phosphor such a porphyrin. This part of the composition acts to provide information on the temperature. The second type of particle is an oxygen permeable polymeric host material such as polymethylmethacrylate in which is occluded a material whose phosphorescence is sensitive to temperature and pressure.

Example 7.

A further suitable paint composition according to the present invention is once again a colloidal suspension in which the colloidal particle is composed of a core of a substantially oxygen permeable polymeric host material such a polymethylmethacrylate, in which is dissolved a

phosphor such as porphyrin and some oxygen. The core is encapsulated with a substantially non-oxygen permeable polymeric host material such as polyvinylidene chloride. This produces double layer particles.

In Examples 6 and 7 the polymethylmethylacrylate was dissolved in a warm organic solvent such as toluene at a temperature in the range of from 50 to 60°C. Porphyrin was added to the solution in an amount of 1mg per millilitre of solution. Other suitable organic solvents include dichloromethane, chloroform, ketones such as propanone, butanone and aromatic solvents such as benzene and toluene. Preferably the phosphorescent material content should be in the range of from 0.1 to 10 milligrammes per millilitre of polymer solution. Apart from porphyrins other suitable phosphorescent materials include neterocyclic dyestuffs and polyaromatic hydrocarbons.

Suitable oxygen permeable polymeric host materials for use in Examples 4 to 7 include polymethyl methacrylate, ethyl cellulose, cellulose acetate and siloxanes. Suitable second phosphorescent materials, preferably inorganic, for use in Examples 4 to 7, include $Y_2 O_2 S$: Eu or YVO_4: Eu.

The foregoing paint compositions according to the present invention are used according to the following methods. The paint compositions of Examples 1 to 3 which are sensitive to changes in temperature have a decay rate of phosphorescence which is longer than the decay rate of

materials sensitive to both temperature and pr ssure. For example if the surface is coated first with a layer of a paint composition according to any one of Examples 1 to 3 and this overcoated with an optically transparent paint sensitive to both temperature and pressure, irradiation of the resulting coating with a laser pulse causes each layer to phosphoresce and the emitted radiation from each layer has a unique decay curve as shown in Figure 1.

A suitable laser pulse length is less than 100 nanoseconds, with a fluence of $10Jm^{-2}$. The wavelength of laser utilised depends on that of the particular phosphor used. For example for porphyrin a frequency doubled Nd-YAG laser at a wavelength of 532 nm is preferred.

Thus in Figure 1 the dashed curve A results from excitation of the paint composition sensitive to temperature only, the dotted curve B is that resulting from excitation of the pressure and temperature sensitive additional coating or part of the original composition and the solid curve C is a composite curve which is the curve actually observed on excitation of the double coated surface or of a surface coated with the composition of Examples 4 to 8 when excited.

The radiation emitted on excitation can be collected in any suitable manner such as by a detector and the observed decay rate C is in fact a superimposition of the decay curves A and B. In Figure 1 I represents intensity

of phosphorescence and t represents time elapsed from excitation.

If the decay rate of the exclusively temperature sensitive coating (a paint composition of Examples 1 to 3) is k_2 then the decay rate of the temperature and pressure sensitive coating or the pressure and temperature component of the composition of Examples 4 to 8 is k_1. If k_1 is very much greater than K_2 then after a suitable time lapse the contribution of curve B to the composite curve C is negligible. This is shown in Figure 1. The value of k_2 can therefore be obtained from the later part of curve C as illustrated and used with the value of k_1 obtained from the earlier part of the curve C to determine both temperature and pressure. Thus for the composite curve C, K_1 is a function of pressure P and temperature T and K_2 is substantially a function of temperature T. The two functions can be solved to provide pressure P and temperature T values.

The rate of decay will vary depending on the part of the decay curve sampled. For this reason all calibrations (and subsequent measurements) are done at the same part of a curve each time. In practice the decay rate is measured as the inverse of the time elapsed between two points on the curve. The two points on the curve will be at fixed fractions of the maximum signal amplitude. Sometimes it may be advantageous to allow a fixed time delay after the

signal peak and call the d layed amplitude the reference amplitude. A fixed time delay would be used to avoid spurious fluorescence or electrical noise at signal peak. In general the rate of decay K will be a function of pressure P and temperature T and in the example above is good for the earlier or upper part of the curve C. The calibration for the lower or later part of the curve C will usually be different but not sufficiently to solve the two functions simultaneously for P and T with any precision. By deliberately introducing a second paint component it is possible to ensure that the two calibration functions are markedly different. This is done by using a second point component with a much lower characteristic decay rate and this is achieved practically by placing the phosphor in an oxygen free environment that is in a formulation which is pressure insensitive.

In the case of the paint compositions of Examples 4 to 8 it is possible for both phosphorescent materials utilised to be sensitive to both temperature and pressure provided that the decay rate - temperature/pressure characteristics of the two materials are sufficiently different for the above described method to be utilised.

CLAIMS

1. A paint composition suitable for application as a coating to a surface, which composition includes a polymeric host material and a phosphorescent material operable to phosphoresce on subjection to irradiation by laser light, with the rate of decay of the intensity of the phosphorescence being a function of the temperature of the irradiated surface.

2. A paint composition according to claim 1, in which the phosphorescent material is dissolved in the polymeric host material, which polymeric host material has a low permeability to oxygen.

3. A paint composition according to claim 2, in which the phosphorescent material is a porphyrin derivative.

4. A paint composition according to claim 2 or claim 3, in which the polymeric host material is polyvinylidene chloride, a co-polymer of vinylchloride and vinyldichloride or polyvinylalcohol.

5. A paint composition according to claim 1, in which the phosphorescent material is suspended in the polymeric host material.

6. A paint composition according to claim 5, in which the phosphorescent material is an inorganic phosphor.

7. A paint composition according to claim 6, in which the inorganic phosphor is yttrium oxysulphide or doped yttrium vanadate.

8. A paint composition according to claim 1, in which the polymeric host material is impregnated with phosphorescent material.

9. A paint composition according to claim 8, in which the polymeric host material is a colloidal suspension of particles of polyvinylidene chloride or a co-polymer of polyvinylchloride and polyvinylidene chloride.

10. A paint composition according to claim 8 or claim 9, in which the polymeric host material is polyvinylalcohol or hydroxy-alkylcellulose.

11. A paint composition according to claim 1, including a second phosphorescent material operable to phosphoresce on subjection to irradiation by laser light, with the rate of decay of the phosphorescence of the second phosphorescent material being a function of the pressure of oxygen over the surface.

12. A paint composition according to claim 11, in which the polymeric host material is permeable to oxygen, in which the oxygen sensitive second phosphorescent material is dissolved in the polymeric host material and in which the temperature sensitive phosphorescent material is suspended in the polymeric host material.

13. A paint composition according to claim 8, in which the the polymeric host material is an oxygen permeable ethylcellulose or siloxane, in which the oxygen sensitive second phosphorescent material is a porphyrin dissolved in the polymeric host material, and in which the temperature

sensitive phosphorescent material is a colloidal suspension of phosphor impregnated particles of polyvinylidene chloride or a co-polymer of polyvinylchloride and polyvinylidene chloride.

14. A paint composition according to claim 11, in which the temperature sensitive phosphorescent material is a low or non-oxygen permeable polymeric material in which is occluded a soluble phosphor, and in which the oxygen sensitive second phosphorescent material is an oxygen permeable polymeric material in which is occluded a material which phosphoresces on irradiation with laser light and has a decay rate which is a function of both temperature of the surface and pressure of oxygen over the surface, with the temperature sensitive phosphorescent material and oxygen sensitive phosphorescent material being a colloidal suspension in said polymeric host material.

15. A paint composition according to claim 14, in which the soluble phosphor is a porphyrin and the oxygen permeable polymeric material is polymethylmethacrylate.

16. A paint composition according to claim 1, in the form of a colloidal suspension of particles having a core of the polymeric host material which is permeable to oxygen in which is dissolved a phosphor and oxygen, which core is encapsulated in a polymeric host material substantially impermeable to oxygen.

17. A paint composition according to claim 16, in which the phosphor is a porphyrin and in which the substantially oxygen impermeable polymeric host material is polyvinylidene chloride.

18. A paint composition suitable for application as a coating to a surface substantially as hereinbefore described with reference to any one of Examples 1 to 8.

19. A method of determining the temperature of a surface, including the steps of applying a coating to the surface of a paint composition according to any one of claims 1 to 10, irradiating the coating with a pulse of laser light, measuring the time for decay of the intensity of the resulting phosphorescence, and relating the decay time to the temperature of the surface.

20. A method of determining the pressure of oxygen over a surface, including the steps of applying a coating to the surface of a paint composition according to any one of claims 1 to 10, applying on top of said coating a further coating of an optically transparent paint composition which phosphoresces on irradiation with laser light and whose time for decay of the intensity of the phosphorescence is a function of both temperature of the irradiated surface and oxygen pressure over the surface, irradiating the two coatings with a pulse of laser light, measuring the time for decay of the intensity of the resulting phosphorescence, at two parts of a plot of the intensity versus time curve, combining this information

with the calibration information for said two parts, and deriving therefrom the oxygen pressure and temperature at the surface.

21. A method of determining the pressure of oxygen over a surface, including the steps of applying a coating to the surface of a paint composition according to any one of claims 11 to 17, irradiating the coated surface with a pulse of laser light, measuring the time for decay of the intensity of the resulting phosphorescence, at two parts of a plot of the intensity versus time curve, combining this information with calibration information for said two parts, and deriving therefrom the oxygen.

22. A method of determining the temperature of a surface as hereinbefore described and as illustrated in Figure 1 of the accompanying drawings.

23. A method of determining the pressure of oxygen over a surface, substantially as hereinbefore described and as illustrated in Figure 1 of the accompanying drawings.